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16. ABSTRACT

The purpose of this study was to compile selected information concerning the manufacture and use of activated carbon, with particular emphasis on product quality as related to the presence of heavy metal ions and/or polynuclear aromatic compounds. Specific areas of interest were the raw materials and methods of production; manufacturers, production capacities, and actual production; types of final products; and consumption patterns of activated carbon. Product quality specifications for heavy metal ions and polynuclear aromatic compounds in the final products were investigated. U.S. production quantities have exceeded 200 million pounds annually for the past 3 to 4 years. Of the estimated 180 million pounds consumed in the United States in 1975, about 37% was employed in food and pharmaceutical areas, 25% in water or waste treatment processes, and 38% in other applications. Activated carbon for use in foods and pharmaceuticals conforms to the Food Chemicals Codex specifications for heavy metal ions and polynuclear aromatics. Products for municipal water treatment are subject to AWWA standards. Activated carbon for other uses are subject only to customer specifications.

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Task IV - Activated Carbon

Contract No. 68-01-3201

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NOTICE

This report has been reviewed by the Office of Toxic Substances, Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency. Mention of tradenames or commercial products is for purposes of clarity only and does not constitute endorsement or recommendation for use.

PREFACE

This report presents the results of Task IV of a project entitled "Chemical Technology and Economics in Environmental Perspectives" performed by Midwest Research Institute (MRI) under Contract No. 68-01-3201 for the Office of Toxic Substances of the U.S. Environmental Protection Agency (EPA). Dr. Irving J. Gruntfest was project officer for EPA.

Task IV, "Activated Carbon," was conducted by Mr. Gary L. Kelso, Associate Chemical Engineer, and Dr. Thomas W. Lapp, Senior Chemist, who is the project leader for this contract. This report was prepared under the supervision of Dr. Edward W. Lawless, Head, Technology Assessment Section. This program had MRI Project No. 4101-L.

MRI would like to express its sincere appreciation to those companies who provided technical information for this report.

Approved for:

MIDWEST RESEARCH INSTITUTE

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SECTION I

INTRODUCTION

The use of charcoal and bone char to decolorize solutions has been employed for centuries but it was not until shortly before World War I that industrial production of activated carbon began in the United States. During World War I, extensive interest in activated carbon developed for use in gas masks as protection against gas warfare. This development provided an impetus for further research and development during subsequent years. These expanded research and development programs not only led to new industrial applications for activated carbon but also introduced new raw materials and activation processes.

At the present time, activated carbon finds widespread usage in the industrial sector. Large quantities are used in the food and beverage industry, particularly for the decolorization of sugar solutions. Other applications in this industry include those for alcoholic beverages, fruit juices, vegetable oils, and many other products. The production of vitamins, hormones, antibiotics, and other pharmaceutical products employs activated carbon. Municipal water treatment plants use activated carbon to remove odors, disagreeable tastes, and impurities from drinking water. In all of the above industries, the majority of the products treated with activated carbon are ingested into the body. Other industries which employ quantities of activated carbon include the dry cleaning industry to remove odors and coloration from spent solvent, the rubber tire reclamation sector to prevent oil staining of white sidewall tires, the electroplating industry, and the general chemical industry for improvement of the purity of products, treatment of wastewater effluents, solvent recovery, gas separation and purification, and catalytic applications.

OBJECTIVES

In view of the widespread and increasing usage of activated carbon in the United States, this brief study was initiated to compile information on various aspects of the manufacture and use of this material. Specifically, the areas of interest were:

1. The raw materials and methods used for the production of each type of activated carbon.

2. Manufacturers and annual production volumes for the past 8 years.

3. Consumption patterns and the approximate quantity consumed in each area.

4. The different grades of final product available from each producer.

5. Product quality specifications with respect to the presence of heavy metal ions and/or polynuclear aromatic compounds in the final product.

6. The procedures used to insure removal of the impurities stated in Item 5.

SECTION II

SUMMARY AND CONCLUSIONS

Activated carbon finds widespread usage in numerous industrial applications and in municipal water treatment. Included in the industrial sector are many uses directly related to products for human consumption, such as sugar, alcoholic beverages, fruit juices, vitamins, hormones, and many others. Municipal water treatment plants use this material to remove odors, disagreeable tastes, and impurities from drinking water.

Because of this widespread consumption of activated carbon and its direct participation in the manufacture of products for human consumption, this brief study was initiated to compile data on various aspects of the production of activated carbon. In addition to market input-output data, e.g., manufacturers, sites, raw materials, production volumes, grades of product, use patterns, etc., this study was conducted to determine the product quality specifications with respect to the presence of heavy metal ions and/or polynuclear aromatic hydrocarbons in the commercial product. If such impurities are present, the procedures used for their removal were to be determined.

The results of the market input-output aspect of this study show that seven companies manufacture commercial quantities of activated carbon in the United States. Of the seven companies, three control about 87% of the total annual capacity of 305 million pounds. This annual capacity is approximately equally split between powdered and granular products. Wood and coal are used quite extensively as raw materials with other materials, e.g., coconut shells, being used in small volumes or for the production of some specialty products. High temperature steam activation is the usual method if coal is the raw material. Wood is normally subjected to the chemical activation process. U.S. production quantities are estimated to have exceeded 200 million pounds annually for the past 3 to 4 years. Of the estimated 180 million pounds consumed in the United States in 1975, approximately 37% was employed in food and pharmaceutical area, 25% in water or waste treatment processes, and 38% in other applications.

Two types of product quality specifications are normally employed for heavy metals and polynuclear hydrocarbons: (a) the Food Chemicals Codex; and (b) specific consumer specifications. Activated carbon intended for use in the food and pharmaceutical industries conforms to the limits set forth in the Food Chemicals Codex. Products to be used in municipal water treatment plants are stated to meet the American Water Works Association (AWWA) specifications; however, these standards do not specify the substances which are unacceptable impurities nor are the maximum acceptable limits for impurities stated. While information concerning individual customer specifications was considered proprietary, it is felt that few of the specifications are directed towards definite limitations on heavy metal ions. Previous studies have shown that, due to the temperatures ($\sim 1000^{\circ}C$) reached during the steam activation process, very little, if any, quantities of polynuclear aromatic hydrocarbons would be retained in the activated carbon. In general, activated carbon for use in the food or pharmaceutical industry or in municipal drinking water is apparently subject to certain limitations on heavy metal content. For other applications, no published data were available and there appears to be few limitations on the content of these impurities.

SECTION III

BACKGROUND INFORMATION

This section discusses the general history, raw materials, activation processes, and uses of activated carbon obtained from literature sources.

GENERAL HISTORY[1,2]

The fact that charcoal adsorbs colors from solutions was known as early as the 15th Century and the first written records which recognized the adsorptive capacity of charcoal in gases and solutions were published in the latter part of the 18th Century. This knowledge was not put to use on an industrial scale, however, until 1811 when Figuier discovered that bone char was more effective than wood char for decolorization. Thereafter, bone char was used extensively for the purification of sugar and other industrial purification needs.

Throughout the 19th Century activated carbon was not produced on an industrial scale since bone char satisfied most of the industrial purification needs during that period, and activated carbon was too difficult to manufacture since the instrumentation necessary to control the critical activation process did not exist. Numerous experiments were conducted on carbon to prepare a product with high adsorptive capacity, and several processes to produce activated carbon were patented during this period of time. It was not until the turn of the century, however, that the industrial development of activated carbon began.

In 1900, Raphael von Ostrejko patented two activation processes and designed the equipment to carry out the processes, thereby laying the foundation for the industrial production of activated carbon. Fanto Works of Vienna adopted one of his processes--the activation of charred materials with steam or carbon dioxide--and produced the first powdered activated carbon, Eponit, in 1909. Norit Company of Amsterdam began production of Norit in 1911 using the same process principles, and Verein fur Chemische und Metallurgische Produktion of Aussig/Elbe began production of Carboraffin in 1913, using a zinc

chloride activation process on wood and other materials of high carbon content that was patented by J. Wunsch in 1913. In America, industrial production of activated carbon began in 1913 with the manufacture of Filtchar, which was improved in 1916 and offered as Superfiltchar, and further improved in 1922 to become Nuchar and Suchar. Production of other American activated carbons after 1913 included Carbrox (1917), Kelpchar (1920), and Darco (1921). The powdered activated carbons produced during this time, in both Europe and America, were intended primarily for decolorizing and purifying raw sugar. Few companies used the activated carbon process prior to World War I, however, since large investments in the bone-char process had already been made, and bone char was already extensively used in the manufacture of sugar.

During World War I, extensive interest in activated carbon developed around its use in gas masks for the protection of soldiers against gas warfare. Since the powdered activated carbons available were unsuitable for gas adsorption, intense research was conducted in Europe and the United States to develop a gas-adsorbing carbon. Granular activated carbons were quickly developed for this purpose, and at the conclusion of the war, further research was conducted on gas-adsorbing carbons to develop important industrial applications, such as odor elimination, recovery of solvent vapors, and benzene extraction from manufactured gas. The research facilities made available by the war effort were also used to experiment with the powdered activated carbons for new applications in liquid purification.

Not only were new applications of activated carbon developed, but new raw materials and new activation processes were found suitable for making activated carbon. Verein in Aussig/Elbe made G-1000, a granular activated carbon with high mechanical strength and adsorptive power for gas and vapor adsorption, from coconut and almond shells using a zinc chloride activation process. They also produced two varieties of pelletized activated carbon, Supersorbon for volatile solvent recovery and Benzorbon for benzene removal from town gas, from sawdust activated by zinc chloride. Bata Company of Czechoslovakia produced a similar product using steam activation. In America, several raw materials were used to produce activated carbon and activation was conducted mainly by steam and phosphoric acid.

RAW MATERIALS[2-5]

Activated carbon can be prepared from a wide variety of carbonaceous raw materials. It has been prepared from materials of vegetable origin such as rice hulls, nut shells, fruit pits, bagasse, cereals, cottonseed hulls, lignin, kelp, coffee beans, corncobs, hardwoods, softwoods, and molasses; from materials of animal origin such as fish, bones, animal flesh, and blood; and from materials of mineral origin such as coal, peat, lignite, petroleum residues, asphalt, carbon black, tars, and pitches. A review of the 1974 and 1975 Chemical Abstracts[3,4] shows that 30 different raw materials, including

some of the above, have been patented as a possible source for activated carbons. These materials are listed below. This listing also includes "older" sources for which new processes have been developed.

Anthracite	Coconut timber	Peat coke
Asphalt	Coking coal	Petroleum pitch
Brown coal	Forest product wastes	Petroleum sludge
Carbon black	Heavy oil-sulfur mixture	Polymer foam
Carbonized black liquor	Kraft pulp waste solution	Sawdust
Cellulose pulp	Lignite	Sugarcane juice foam
Charcoal	Lignite char and limestone	Swine manure
Coal and polystyrene	Peat	Waste tires
Coal tar	Olive stones	Wood waste
Coconut shells	Novalak (a phenol-formaldehyde type resin)	

Within recent times, most of the activated carbons produced for liquid phase applications are made from bones, wood, peat, lignite, and lignin (paper per mill waste), and most of the material produced for gas adsorption are made from coal, peat, coconut shells, and petroleum residues. Activated carbon production is generally limited to these raw materials for economic reasons.

ACTIVATION PROCESSES[1,5-7]

The activated carbon industry employs a variety of processes to produce activated carbons. A number of activation methods are currently used and may be divided into two categories: physical activation and chemical activation. General descriptions of these activation methods are discussed below.

Physical Activation

Activation processes that fall into this category use a gaseous substance as the activating agent or simply carbonize the raw material into the final product. When a gaseous substance is used, the process is conducted in two steps: carbonization and activation. The carbonization step consists of heating the raw material to temperatures of 600°C in the absence of air (called calcining) to convert the material to primary carbon. The pores of the resulting intermediate carbon are generally either too small or too constricted with decomposition products and tars to be a useful material. This intermediate carbon is then reacted with a gaseous substance (usually steam) as the activating agent at a high temperature (~ 1000°C) to drive off the decomposition products and tars and to enhance the pore structure of the carbon. A one-step process is sometimes used wherein the raw material, such as bone char, is carbonized at a high temperature to produce a suitable product without further treatment.

Activation methods which oxidize the carbon under controlled conditions may employ steam, carbon dioxide, or air. The steam activation process is by far the most widely and extensively used physical activation process in the activated carbon manufacturing industry. The steam activation step consists of reacting the carbon intermediate with steam at temperatures between 900 and 1000°C. Activation with carbon dioxide, used to a limited extent, generally consists of using flue gas which contains some steam as the activating agent. This process involves a less energetic reaction than that with steam and generally requires a higher temperature of 900 to 1100°C. Activation with air is conducted at lower temperatures of 300 to 600°C, but is rarely used since the process is beset with certain difficulties, such as high carbon losses, nonuniform activation, and temperature control problems.

A one-step physical activation process is used for bone char wherein crushed and degreased bones are heated indirectly in steel retorts at temperatures between 750 and 950°C. The carbonized bones are then suitable for use as a final activated carbon product.

Chemical Activation

Activation processes that fall into this category use a chemical substance as the activating agent. Chemical activation is used almost exclusively for carbons produced from wood, although it has been used on other raw materials such as peat. The advantage of chemical activation is that formation of tars and aqueous distillate during carbonization is minimized, and lower temperatures are generally required for activation of the carbon.

The carbonaceous raw material is usually mixed with the chemical activating agent in a concentrated solution prior to carbonization (although occasionally impregnation of the carbon with the chemical will be performed after carbonization). The chemically treated raw material is then carbonized at a low temperature of about 400 to 500°C. After carbonization, the carbon intermediate is calcined at 500 to 900°C to achieve pyrolytic decomposition. The carbonized product is then removed from the kiln, cooled, and washed to remove and recover the activating agent from the activated carbon.

Phosphoric acid and zinc chloride are the most widely used activation agents. Occasionally dolomite, sodium sulfate, sodium phosphate, potassium sulfide, potassium thiocyanate, hydroxides of alkali metals, and other chemicals are used in various processes.

Combination Activation Processes

Both chemical and physical activation processes can be combined different ways to form a single activation process. Sometimes activated carbon produced by chemical activation is treated further with high temperature

steam to increase the number of wider pores or to remove substances that have fouled the pores during the normal chemical activation process. Other combinations of the basic processes described above are possible, when the need arises, to produce activated carbons of particular quality.

USES

Activated carbon is used throughout industry for many liquid phase and gas phase applications. Liquid phase applications are subdivided into two major categories: (a) liquid purification, and (b) solute removal for recovery. Liquid purification involves removing impurities which cause objectionable colors, tastes, odors, foaming, or crystal retardation. Solute removal for recovery involves adsorption and subsequent elution of the solute. Gas phase applications are subdivided into three major categories: (a) solvent recovery, (b) gas purification or separation, and (c) catalytic applications. Solvent recovery involves adsorbing the solvent from a gas stream, and recovering the solvent from the activated carbon. Gas purification and separation involves adsorbing impurities from a gas stream or adsorbing valuable constituents for recovery. Catalytic applications involve the use of activated carbon as the catalyst for oxidation of inorganic and organic compounds, or as a catalyst carrier.[5/]

Both powdered and granular forms of activated carbon are manufactured in a wide variety of grades and sizes to accommodate the various liquid and gas phase applications. The powdered form is made for liquid phase applications only, and is generally ground down to particle sizes in the range of 5 to 100 μm, although other sizes are available. This form of carbon is added to the liquid being treated, intimately mixed with the liquid in standard chemical plant equipment such as stirrers and tanks, and then filtered or settled out of the liquid to remove the impurities or solute for recovery. The granular form is made for both liquid and gas phase applications, and is produced in various grades with particle sizes ranging from 0.25 to 4 mm. This form of activated carbon is used in columns, towers, or filters, and the fluid is passed through it for purification, separation, solvent recovery, or catalytic applications. Regeneration of granular activated carbon for reuse is normally conducted to make the operation economical.[7/]

A description of the various uses of activated carbon follows and the current quantitative use pattern is discussed in Section IV.

Liquid Phase Applications

Purification of liquids with activated carbon is conducted in the food and beverage industry, in municipal water treatment plants, in the dry cleaning industry, in the rubber tire reclamation industry, in the chemical industry, and throughout industry in general for wastewater effluent treatment and miscellaneous reasons. Solute removal for recovery is conducted in the pharmaceutical industry.

Food and Beverage Industry - Activated carbon is used extensively in the sugar industry to decolorize sugar solutions. Though color removal is the prime objective, nitrogenous substances and lyophillic colloids are also removed by the carbon. Removal of these substances improves the sugar manufacturing process by increasing the speed of crystallization, reducing foaming in the evaporators, and improving the filterability of the liquor.[5]

Many other food and beverage products are treated with activated carbon to remove color, unpleasant taste, disagreeable odors, and colloidal impurities that cause turbidity or cloudiness. Some of the products treated include alcohol, beer, coloring, fruit juice, gelatin, honey, lard, reclaimed candy syrups, vegetable oils, wine, yeast, meat extracts, whiskey, vinegar and pectin.[5-7]

Municipal Water Treatment Plants - Removal of disagreeable odors, disagreeable tastes, and harmful impurities in drinking water has been successfully achieved with activated carbon.

Dry Cleaning Industry - Solvents used in dry cleaning plants and coin-operated dry cleaning machines rapidly become contaminated with oils, greases, and bleeding dyes as they remove the soil from clothes. Activated carbon is used extensively in this industry to remove the odors and colors from spent solvent so that it can be reused.[5]

Rubber Tire Reclamation Industry - The process of reclaiming rubber introduces oils into the rubber which make it unfit for use in the manufacture of white sidewall tires, since the oil migrates to the outer ply and stains the white rubber during tire manufacture. Activated carbon powder is milled into the reclaimed rubber to immobilize the oil, and make the reclaimed rubber fit for use.[5]

Chemical Industry - Many chemical manufacturing processes employ activated carbon to simplify the process and improve the purity of the chemical product. Examples of chemicals treated with carbon are detergents, dyestuff intermediates, glycerine, monosodium glutamate, organic acids, organic intermediates for optical brighteners, photographic chemicals, plasticizers, shellac, technical alcohol, glycols and alkaloids.[5-7]

Pharmaceutical Industry - Vitamins, hormones, antibiotics, medicinal tablets, and many other pharmaceuticals are made with the aid of activated carbon. The carbon is used in a dilute broth to extract the biochemical which is subsequently eluted from the carbon with a suitable solvent. This solvent is then distilled or treated with an immiscible solvent to recover or concentrate the biochemical. Penicillin, streptomycin, and other antibiotics have been separated and purified on a large scale in this manner.[5]

Electroplating Industry - Activated carbon has been used to remove impurities and to recover valuable constituents, such as gold, from electroplating baths.

Industry in General - Purification of wastewater effluent from manufacturing plants and other industrial operations represents a significant useage of activated carbon. It has been found useful in removing various impurities and contaminants from wastewater generated by pesticide manufacturers and formulators, dyeing and textile mills, acid mine drainage operations, cardboard and paper mills, photographic processing plants, and paint and printing ink manufacturers, just to name a few examples. The carbon's role in preventing environmental pollution from contaminated wastewater effluent may be large in the future, and this market represents a large potential use of activated carbon.[4]

Gas Phase Applications

Activated carbon has a wide range of uses for gas phase applications. In industry it is used primarily in solvent recovery and in gas purification and separation, with some uses as a catalyst or catalyst carrier. It is also used extensively in the home and commercial establishments for air purification. Some of the important gas phase uses are described below.

Solvent Recovery - Probably the most important use of activated carbon in gas phase applications is the recovery of volatile organic solvents from air in industrial manufacturing plants. A carbon recovery system, consisting of two carbon beds, an air filter, a blower, a vapor condenser, and a solvent decanter or continuous still, receives the vapor-laden air from the manufacturing process, and the carbon adsorbs the volatile solvent. The solvent is then removed from the carbon by low-pressure steam and the steam-solvent mixture is condensed. The condensate is then either decanted or distilled to recover the solvent.[5]

There are hundreds of operating plants recovering billions of pounds of solvent each year with an activated carbon recovery system. The solvents recovered are valued in the hundreds of millions of dollars, and represent a substantial economic saving to those industries using this practice. In

addition to economic considerations, solvent recovery operations prevent the escape of volatile solvents into the atmosphere and thereby act as pollution control systems.[8]

Some typical industries which use activated carbon solvent systems to recover valuable solvents and/or prevent air pollution by the solvents include:[5-8]

Industry	Solvent (or gas) recovered
Acetate fiber	Ketones
Rotogravure printing	Acetates, alcohols, hydrocarbons
Rubber production	Hydrocarbons, chlorinated solvents
Metal degreasing	Chlorinated and fluorinated solvents
Paper, fabric, and plastic film coating	Ketone, acetates, hydrocarbons
Cellulose acetate rayon	Acetone
Plastic manufacture	Alcohols, esters, ketones, hydrocarbons
Nitrocellulose silk	Ether, alcohol

Gas Purification and Separation - Gases are often purified by passing the gas through a two-bed system consisting of two tall vertical towers containing activated carbon. The carbon adsorbs the impurities in the gas, and is then thermally regenerated for reuse. Some typical industrial applications for gas purification are: purification of hydrogen from cracking operations for use in ammonia synthesis; deodorization of carbon dioxide to be used in dry ice manufacture; removal of objectionable organic sulfur compounds from acetylene intended for synthesis; removal of pyridine from ammonia to be oxidized into nitric acid; removal of hydrogen sulfide and organic sulfur from natural and manufactured gas; removal of oil vapor from compressed air and gases; and purification of gases for critical chemical, pharmaceutical, and food processes.[5,8]

The purification of air by removing odors, tastes, and other impurities with activated carbon filters is widely employed. Carbon filters are used in gas masks, air-conditioning units, ventilation systems, home kitchens, laboratories, etc. to clean and purify atmospheric air.

Gas separation can also be achieved with an activated carbon system. A typical example is a tall, vertical-column, moving-bed system for separating light hydrocarbon gases from lean gas streams.[5]

Catalytic Applications - Activated carbon can act as a catalyst in the oxidation of inorganic and organic compounds. Some typical applications of carbon as an oxidizing catalyst are for ferrous sulfate, sodium arsenite, potassium nitrite, and potassium ferrocyanide oxidations.[5]

Some other typical industrial operations which take place in the presence of carbon as a catalyst are hydrogen peroxide decomposition, hydrogen sulfide oxidation to sulfur, phosgene manufacture from carbon monoxide and chlorine, and sulfuryl chloride manufacture by the reaction of sulfur dioxide with chlorine.[5]

Activated carbon is used as a catalyst support in the manufacture of vinyl chloride (by reaction of acetylene and hydrogen chloride in the presence of carbon impregnated with barium chloride and/or mercuric chloride), and in the manufacture of vinyl acetate (by reaction of acetylene and glacial acetic acid in the presence of carbon impregnated with zinc acetate). It is also used as a catalyst support in the manufacture of trichloroethylene, fluorocarbons, and in many hydrogenation operations.

REFERENCES

1. Smisek, M., and S. Cerny, Active Carbon: Manufacture, Properties, and Applications, Elsevier Publishing Company, New York (1970).

2. Kirk, R. E., and D. F. Othmer, Encyclopedia of Chemical Technology, Interscience Publishing Company, New York, Vol. 2 (1948).

3. Chemical Abstracts, 81 (1974).

4. Chemical Abstracts, 82 (1975).

5. Kirk, R. E., and D. F. Othmer, Encyclopedia of Chemical Technology, Interscience Publishing Company, New York, 2nd Ed., Vol. 4 (1964).

6. U.S. Environmental Protection Agency, Process Design Manual for Carbon Adsorption, Technology Transfer, October 1973.

7. Introduction to Activated Carbon, Norit-Clydesdale Company, Ltd., Glasgow, United Kingdom (current company publication).

8. Columbia® Activated Carbon: The Capability Carbon, Union Carbide Corporation, Riverside Plaza, Chicago, Illinois (1973).

SECTION IV

CURRENT INDUSTRIAL DATA

The activated carbon industry in the United States consists of seven manufacturers, each of which produce quantities of activated carbon products from different raw materials and using different activation processes. Many grades and types of products are made for a wide variety of uses and applications for industry, business, and the home.

This section of the report presents current data for the activated carbon industry and the methodology used to obtain this information. The data include information on the manufacturers; production quantities; raw materials and activation processes; grades, types, and uses of individual products made by each manufacturer; quantities used in the U.S. by use category; and product specifications as related to the presence of heavy metal ions and polynuclear aromatic compounds.

METHODOLOGY OF DATA COLLECTION

The current data for the activated carbon industry given in this section of the report were obtained from four primary sources: (a) published literature; (b) product literature from the manufacturers; (c) telephone interviews and correspondence with representatives of the manufacturers; and (d) telephone interviews with other knowledgeable persons. The literature search was conducted to obtain information on the manufacturers, production quantities, and use pattern of activated carbon; these sources are given in the references at the end of this section. In addition to these sources, other sources, including Chemical Abstracts, the Biennial Conferences on Carbon, an NTIS bibliography on activated carbon (221 references), and recent books in the subject area were reviewed. These other sources provided no useful information related to the analysis for, or studies on, the presence of heavy metal ions or polynuclear aromatic compounds in activated carbon. Data presented on the raw materials, activation processes, and product grades, types, and uses, were obtained from product literature of the manufacturers, the telephone interviews, and correspondence. These sources were also used to supplement and confirm the data obtained from the literature search.

MANUFACTURERS

Activated carbon is manufactured in the United States by seven companies at eight plant sites. Three of the manufacturers--Westvaco Corporation, Calgon Corporation, and ICI United States, Inc.--have a total estimated annual capacity of 265 million pounds, or about 87% of the total industry capacity of 305 million pounds. Table 1 lists the manufacturers, their plant sites, their respective capacities, and the estimated capacities to produce granular and/or powdered activated carbon.

American Norit Company does not currently produce activated carbon in the United States. They prepare specialty products from material imported from their manufacturing facilities in the Netherlands and Scotland.[1] The Carborundum Company is currently producing activated carbon only for testing and evaluation purposes.[2]

PRODUCTION QUANTITIES

The quantities of activated carbon produced in the United States for decolorizing and water purification purposes during the time interval 1967 to 1975 are shown in Table 2. Estimated imports and exports of all types of activated carbon are also given for the same time period.

In addition to the quantities of material produced for decolorizing and water purification purposes, activated carbon was also produced during 1967 to 1975 for gas phase applications. These quantities are not included in the governmental reports. Industrial sources would not divulge the actual quantities produced for gas phase applications and would state only a percentage range of 5 to 15% for 1965 to 1970 and 15 to 20% for 1971 to 1975.[5] These figures are percentages of the quantities produced for decolorizing and water purification grades.

RAW MATERIALS AND ACTIVATION PROCESSES

The activated carbon industry uses various raw materials and activation processes to produce a wide variety of products. The raw materials and activation process used for each raw material are given in Table 3 for each of the seven manufacturers, along with the source of the information.

Table 1. CURRENT U.S. MANUFACTURERS OF ACTIVATED CARBON

Company	Site	Annual capacity ($\times 10^6$ lb)[a]	Granular[b]	Powder[b]
American Norit Company, Inc.	Jacksonville, Florida	NA	(Imported)	
Barnebey-Cheney Company	Columbus, Ohio	10	10 (est.)	
Carborundum Company Refractories and Electronics Division	Niagara Falls, New York	NOS[c]	Will be all granular	
Husky Industry, Inc. Division of Husky Oil Company	Romeo, Florida	20	-	20
ICI United States, Inc.	Marshall, Texas	75[d]	≤ 15	≥ 60
Calgon Corporation Division of Merck and Company, Inc.	Catlettsburg, Kentucky Neville Island, Pennsylvania	90	90	Small as by-product
Union Carbide Corporation	Fostoria, Ohio	5	5[e]	-
Westvaco Corporation	Covington, Kentucky	100	30	70
Witco Chemical Corporation	Petrolia, Pennsylvania	5	5	-
Total		305	≤ 155	≥ 150

a/ "Directory of Chemical Producers," Stanford Research Institute, 1976 edition; and manufacturers estimates (Reference 3).

b/ Reference 4 and manufacturer's estimates.

c/ Not on stream.

d/ A recent article in Chemical Marketing Reporter (1-31-77; p. 4) states that ICI will install a new kiln for both granular and powdered forms. The kiln is scheduled to be on stream in 1979 and increase plant capacity by 40%.

e/ Includes extruded forms of activated carbon.

Table 2. PRODUCTION OF ACTIVATED CARBON, 1967-1975

Year	U.S. production[a] ($x10^6$ lb)	Imports[b] ($x10^6$ lb)	Exports[b] ($x10^6$ lb)
1967	166.2	5.3	18.3
1968	169.0	5.3	20.0
1969	170.0	4.4	18.6
1970	159.6	4.7	22.9
1971	166.0	5.0	26.7
1972	166.9	5.0	29.0
1973	168.4	6.9	39.5
1974	176.7	11.0	45.2
1975 (est.)	151.8	13.2	31.7

a/ Decolorizing and water purification grades only; U.S. Department of Commerce/Bureau of the Census data from "Current Industrial Reports - Inorganic Chemicals."

b/ Estimated quantities calculated from dollar figures supplied by U.S. Department of Commerce/Bureau of Domestic Commerce. These quantities are for all grades of activated carbon (Reference 6).

Table 3. RAW MATERIALS AND ACTIVATION PROCESSES USED TO PRODUCE CARBON, BY MANUFACTURER

Manufacturer	Raw material	Activation process	Reference
Westvaco	Coal	Thermal	7
	Wood	Chemical	
Calgon	Coal	High-temperature steam	4,5
	Coconut shell	High-temperature steam	
ICI	Lignite	High-temperature steam	8
	Wood	Phosphoric acid	
	Carbonaceous material	High-temperature steam	
Husky Oil	Unknown[a]	Unknown[a]	
Barnebey-Cheney	Unknown[b]	Unknown[b]	
Witco	Miley coke	Unknown[c]	9
Union Carbide	Coal	High-temperature selective oxidation	10
	Petroleum coke		
	Coconut		

a/ Husky Oil did not respond to written correspondence.
b/ Barnebey-Cheney did not respond to telephone interviews or correspondence.
c/ Witco would not divulge its activation process.

PRODUCT TYPES, GRADES, AND USES

The activated carbon industry produces a wide variety of products for many applications in industry, business, and the home. Each manufacturer produces a number of types and grades of products for applications in various markets. Table 4 shows the types, grades, and uses of the major activated carbon products made by five of the manufacturers and American Norit Company, Inc., which imports all of its products from abroad. The table was constructed from information obtained from References 1, 5, and 7 through 10.

CONSUMPTION PATTERN

Uses of the numerous types and grades of activated carbon compiled from the manufacturer's specification sheets were presented in the previous subsection and in Section III. Table 5 shows the consumption of activated carbon in the United States for 1972 and estimated figures for 1975. Estimated figures are based on information obtained from certain manufacturers. The tabulated figures do not include those quantities exported.

The miscellaneous category includes uses in the chemical industry for the production of detergents, glycerine, monosodium glutamate, phenol, soda ash, organic acids, photographic chemicals, plasticizers, glycols, and numerous other chemicals.

PRODUCT SPECIFICATIONS

Activated carbon products have different physical and chemical properties that depend upon the raw materials from which they are made, and upon the manner in which they are produced and processed. The raw material, activation process, and additional processing chosen for the manufacture of a particular grade and type of activated carbon depends primarily upon its intended application, and the specifications to which the product is made.

Products made for general uses, such as most gas phase applications, are normally made to general specifications such as mesh size, apparent or bulk density, carbon tetrachloride activity, percent moisture, percent ash, hardness, retentivity, total surface area, total pore volume, void volume, molasses number, and iodine number. Product bulletins from manufacturers give the values of many of these general characteristics of their products. Values reported as "typical" (or general) characteristics are normally determined only occasionally, and are usually not guaranteed by the manufacturer. Values reported as "specifications" are determined by routine and frequent testing, and are generally controlled parameters in the production process.[7-10]

Table 4. ACTIVATED CARBON PRODUCTS: TYPES, GRADES, AND USES, BY MANUFACTURER

Manufacturer	Type	Grade	Mesh size(s)a/	Use(s)
Westvaco	Powdered	Nuchar® S-A	Through 100, Through 200, Through 325	Industrial decolorizing
		Nuchar® S-N	Through 100, Through 200, Through 325	Industrial decolorizing
		Aqua Nuchar®	100, 200, 325	Water treatment
		Filtchar®	100, 200, 300	Water treatment
	Granular	Nuchar® WV-W	8 x 30, 12 x 40, 14 x 40, 20 x 50	Industrial and municipal water treatment
		Nuchar® WV-L	8 x 30	Corn syrup and sugar processing, purification of chemicals and pharmaceuticals, and waste water treatment
		Nuchar® WV-G	12 x 40	Purification and processing of chemicals and pharmaceuticals, and waste water treatment
		Nuchar® WV-H	4 x 8, 4 x 10, 6 x 16	Vapor phase applications such as solvent recovery, odor removal, respirators, air conditioning, cigarette filters, air pollution control, and catalysts or catalyst support
ICI	Powdered	Darco® S-51	98% Through 100, 70% Through 325	Many liquid purification applications
		Darco® G-60	95% Through 100, 70% Through 325	Removes inorganic contaminants from liquids
		Darco® KB	99% Through 100, 70% Through 325	Decolorize liquids
		Darco® BG	98% Through 100, 70% Through 325	Beer production and treatment
		Darco® GFP	95% Through 325	Removal of flotation reagents and metallic ions from ore pulps and concentrates in mineral processing industry
	Granular	Granular Darco®	4 x 12, 12 x 20, 12 x 40, 20 x 40	Continuous column percolation purification of sugar, pharmaceuticals, organic acids, and other foods and chemicals
Witco	Granular	Witcarb® 940	4 x 10, 8 x 30, 12 x 30, 14 x 40, 50 x 140	Gas phase applications
		Witcarb® 950	4 x 10, 6 x 12, 8 x 30, 12 x 30, 18 x 40, 50 x 140, 80 x 325	
		Witcarb® 960	4 x 10, 6 x 12	
		Witcarb® 965	8 x 16, 12 x 20	
Union Carbide	Extruded pellets	Columbia® MSQ	4 x 6, 6 x 8, 8 x 10	Gas phase applications such as solvent recovery, air conditioning, and catalyst carrier
		Columbia® MST	4 x 6, 6 x 8	
		Columbia® MSV	4 x 6, 6 x 8, 8 x 10	
Calgon Corpora-	Powdered	RB	65 to 85% through 325	Decolorizing, purification, and isolation of chemical, pharmaceutical and food products. Types RL and C used primarily with light colored liquids.
		RC		
Activated Carbon)		RL		
		C		
	Granular	PCB	4 x 10, 6 x 16, 12 x 30 plus 6 special sizes	Vapor phase applications such as solvent recovery; precious metal catalyst support.

Table 4 (Concluded)

Manufacturer	Type	Grade	Mesh size(s)[a]	Use(s)
American Norit (All imported)	Powdered	BPL	4 x 10, 6 x 16, 12 x 30 plus 4 special sizes	Vapor phase application such as solvent recovery; catalyst support for production of vinyl chloride and vinyl acetate monomers; hydrocarbon separation; other miscellaneous applications.
		RFX	12 x 30	Vapor phase application such as evaporative emissions control.
		SGL	8 x 30	Corn sugar purification decolorization and purification of numerous products in chemical and food process industries.
		CAL	12 x 40	Beet sugar refining, decolorization and purification of numerous aqueous and organic liquids.
		CPG	12 x 40	Liquid phase applications.
		Norit® EX Norit® A Norit® SS	Unspecified	Purification of plating solutions and chemical intermediates, decolorization of vegetable oils and fats, glycerin, and plasticizers
		Norit® FQA Norit® F Norit® EXW		Treatment of products of high purity in critical applications
		Norit® SG Extra Norit® SG Norit® 211 Norit® SG II	Unspecified	Decolorization of wine, plasticizers, and fine chemicals Liquid sugar refining, bleaching, fatty acids and esters, bleaching vegetable oils and fats, and conditioning of beer
		Polycarbon C	Unspecified	Bleaching glycerin, purification of amine solutions used in gas desulfurization, and water treatment
		Norit® EN-4	96 to 100% Through 100, 60 to 65% Through 325	
	Granular	Norit®	4 x 14, 8 x 20, 14 x 60	Wide range of industrial processes for such applications as gas or vapor phase adsorption, gas separation, and catalysis
	Extruded pellets	Norit® RB1	16 x 20	
		Norit® RB2	8 x 12	
		Norit® RB3	6 x 8	
		Norit® RB4	4 x 6	

a/ U.S. standard sieve.
Sources: References 1, 5 and 7 through 10.

Table 5. CONSUMPTION OF ACTIVATED CARBON IN 1972 AND 1975

Area	Quantity ($\times 10^6$ lb) 1972[a]	1975[b]
Sugar decolorizing	50	50
Water treatment	34	35
Waste treatment	4	7
Gas phase applications	32	34
Pharmaceutical uses	8	8
Foods, beverages, fats, oils	7	8
Dry cleaning	6	7
Electroplating industry	3	4
Reclaimed rubber	3	4
Miscellaneous	20	23
Total	167	180

a/ Data from Reference 8.

b/ Estimated figures based on information from manufacturers.

Products made to the general specifications described above are not normally subjected to quality controls that specifically limit the quantities of impurities in the product, nor to laboratory tests that determine the levels of impurities present. For example, information received from Union Carbide and Witco Chemical Corporation indicates the typical specifications to which activated carbons intended for general uses are made.

Union Carbide manufactures products for gas-phase applications such as solvent recovery, air conditioning filters, and catalytic processes, and tests the products for the following properties: mesh size, apparent density, carbon tetrachloride activity, percent moisture, hardness, percent ash and retentivity. Their products are not manufactured to any other specifications than those given here, and the tests performed to determine these characteristics do not determine the amounts of impurities in the products.[10]

Witco Chemical Corporation manufactures products for gas-phase applications and does not make their products to any particular specifications. Their product bulletins show the six typical characteristics of their products: mesh size, apparent density, carbon tetrachloride activity, percent moisture, percent ash, and surface area. The first three characteristics are determined by tests while the latter three characteristics are neither tested nor guaranteed by Witco, but merely represent typical values for their products.[9]

Products made for food, pharmaceutical, or drinking water applications, however, are manufactured to more rigid specifications which are routinely and frequently tested and maintained by quality controls in the production process. Products used in municipal water treatment are manufactured to the specifications of the American Water Works Association Standard for Powdered Activated Carbon, or the American Water Works Association Standard for Granular Activated Carbon; those used in foods and beverages are manufactured to the specifications of the Food Chemicals Codex or customer specifications; and those used in other applications, such as pharmaceuticals, that require high-purity activated carbon are manufactured to customer specifications.

The AWWA standards do not specify the substances which are unacceptable impurities in activated carbons used in municipal water treatment, nor do they specify maximum acceptable limits for impurities. The AWWA Standard for Powdered Activated Carbon states:

"The powdered activated carbon supplied under this standard shall contain no soluble mineral or organic substances in quantities capable of producing deleterious or injurious effects upon the health of those consuming the water, or that would otherwise render unfit for public water supply use the water, which has been treated properly with the powdered activated carbon."[11]

The Food Chemicals Codex specifies limits on impurities in the activated carbon in the following manner:[12] Water extractables shall not exceed 4%; arsenic (as As) shall not exceed 3 ppm; heavy metals (as Pb) shall not exceed 40 ppm; lead shall not exceed 10 ppm; higher aromatic hydrocarbons shall pass the test; and cyanogen compounds shall pass the test.

The test procedures are given in detail in the Food Chemicals Codex[12] and are either quoted* or summarized as follows:

1. Water extractables test: "Transfer 5.00 g of the sample into a 250-ml flask provided with a reflux condenser and a Bunsen valve. Add 100 ml of water and several glass beads, and reflux for 1 hr. Cool slightly, and filter through Whatman No. 12 or equivalent filter paper, discarding the first 10 ml of filtrate. Cool the subsequent filtrate to room temperature, and pipet 25.0 ml into a tared crystalization dish. (Note: Retain the remainder of the filtrate for the arsenic, heavy metals, and lead tests.) Evaporate the filtrate in the dish to incipient dryness on a hot plate, never allowing the solution to boil. Dry for 1 hr at 100 in a vacuum oven, cool, and weight."

2. Arsenic test: Test a 20-ml portion of the filtrate from the water extractables test, diluted to 35 ml with water, using the silver diethyldithiocarbamate colorimetric method.

3. Heavy metals test: Test a 10 ml portion of the filtrate from the water extractables test (using 20 mcg of lead ion (Pb) in the control solution) for the common metallic impurities Ag, As, Bi, Cd, Cu, Hg, Pb, Sb, and Sn. Details of the test are given on pages 920 to 923.

4. Lead test: Test a 20-ml portion of the filtrate from the water extractables test (using 10 mcg of lead ion (Pb) in the control) using the lead limit test given on pages 929 to 930.

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5. Higher aromatic hydrocarbons: "Extract 1 g of the sample with 12 ml of cyclohexane in a continuous-extraction apparatus for 2 hr. The extract shows no more color and not more fluorescence than does a solution of 100 mcg of quinine sulfate in 1,000 ml of 0.1 N sulfuric acid when observed in ultraviolet light."

6. Cyanogen compounds: "Mix 5 g of the sample with 50 ml of water and 2 g of tartaric acid, and distil the mixture, collecting 25 ml of distillate below the surface of a mixture of 2 ml of sodium hydroxide T.S. and 10 ml of water contained in a small flask placed in an ice bath. Dilute the distillate to 50 ml with water, and mix. Add 12 drops of ferrous sulfate T.S. to 25 ml of the diluted distillate, heat almost to boiling, cool, and add 1 ml of hydrochloric acid. No blue color is produced."

Customer specifications vary as to their requirements for the purity of the activated carbon the customer purchases, and each limits the impurity content of the activated carbon based upon the operation for which it is used.

PRODUCT IMPURITES

Metal ions and polynuclear aromatic hydrocarbons are potential impurities in all activated carbon products. There were no published data available that specified the degree to which activated carbons may be contaminated by these impurities, but telephone interviews with manufacturers revealed two important points: (a) most general use activated carbon products are not specifically tested for these impurities; and (b) tests for these impurities have been performed by some manufacturers and buyers, but these data are not available.

Most products do not require specifications that limit their metal ion and polynuclear aromatic hydrocarbon content, and are either tested only occasionally, or not at all, for these constituents. Only those products made to the Food Chemicals Codex specifications, or to customer specifications which set upper limits on these impurities, are routinely tested for the qualitative and quantitative amount of these impurities.

Telephone interviews with industry representatives[7,8] indicate that most arsenics and organic materials are destroyed or driven off at the temperatures of activation (about 1,000°C), and that metal ions are not normally a problem contaminant. In 1961 an examination of fresh activated carbon did not show the presence of polynuclear aromatic hydrocarbon and later studies indicated that, in this respect, the carbon was suitable for use in water treatment.[13] Activated carbons produced for the food industry are routinely tested by both the manufacturer and the buyers for these impurities, and neither the manufacturer nor the buyers have found constituents in the carbon which they felt were detrimental to human consumption.

This does not mean, however, that all products meet the heavy metals and higher aromatic hydrocarbons specifications found in the Food Chemicals Codex. If the manufacturer should determine that a batch of activated carbon contained impurities above the limits specified by the Food Chemicals Codex or customer specifications, the product would not be sold for the intended usage. Instead, the product could be reprocessed, or sold for uses that require less severe specifications.

In actual practice, the manufacturers would perform very little reprocessing of off-specification products, and would simply sell these products for more general uses that have fewer specifications. For example, granular products which do not meet the hardness specifications can be pulverized and sold as powdered products, or products which do not meet the activity specifications can be sold as lower grades which have lower activity specifications. If any products were to exceed the specification limits for hydrocarbons and/or metal ions, they could be sold for uses for which metal ion and hydrocarbon specifications do not exist.

Without laboratory and test data, it is impossible to determine the qualitative and quantitative amounts of impurities in the form of metal ions and polynuclear aromatic hydrocarbons (if any) that exist in activated carbon products. This data does exist in some cases but was not available for this study. For example, one company has performed numerous laboratory tests to determine the heavy metal content of their own products and competitors' as well, and has hired independent laboratories to test these products. The tests involve both qualitative and quantitative determinations of the metals present in the products. Data regarding these tests are not strictly proprietary since some of them are given to buyers of their products (especially in the food industry) but were not available for this study.

REFERENCES

1. Correspondence with American Norit Company, Inc., Jacksonville, Florida.

2. Correspondence with Carborundum Company, Niagria Falls, New York.

3. Stanford Research Institute, Directory of Chemical Producers, 1976 Edition, Menlo Park, California (1976).

4. Chem. Eng. News, p. 7, July 22, 1974.

5. Telephone interview and written response from Calgon Corporation, Pittsburgh, Pennsylvania.

6. Maxey, F., U.S. Department of Commerce, Bureau of Domestic Commerce, Washington, D.C.

7. Correspondence and telephone interviews with Westvaco Corporation, Chemical Division, Carbon Department, Covington, Virginia.

8. Correspondence and telephone interviews with ICI United States, Inc., Speciality Chemicals Division, Wilmington, Delaware.

9. Correspondence and telephone interviews with Witco Chemical Corporation Inorganic Specialties Division, New York, New York.

10. Correspondence and telephone interviews with Union Carbide Corporation, Carbon Products Division, Cleveland, Ohio.

11. Gullans, O., M. S. Nichols, and C. M. Bach, AWWA Standard for Powdered Activated Carbon, AWWA B600-66, American Water Works Association, Denver, Colorado (1966).

12. Food Chemicals Codex, Prepared by the Committee on Specifications, Food Chemicals Codex, of the Committee on Food Protection of the National Research Council, National Academy of Sciences, Washington, D.C. (1972).

13. Andelman, J. B., and M. J. Suess, Bull. World Health Org., 43, 495 (1970).